



Short communication

PbO₂-modified graphite felt as the positive electrode for an all-vanadium redox flow battery



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ABSTRACT

A novel approach for enhancing the electrochemical performance of graphite felt electrodes by employing non-precious metal oxides is designed for an all-vanadium redox flow battery (VRFB). Lead dioxide (PbO₂) is prepared through pulse electrodeposition method and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical performance of the prepared electrode is evaluated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Results show that PbO₂ exhibits excellent electro-catalytic activity and reactive velocity to vanadium redox couples. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the vanadium redox flow battery with as-prepared electrodes at 70 mA cm⁻² are 99.5%, 82.4%, and 82.0%, respectively; these values are much higher than those of a cell assembled with bare graphite felt electrodes. The outstanding electro-catalytic activity and mechanical stability of PbO₂ are advantageous in facilitating the redox reaction of vanadium ions, leading to the efficient operation of a vanadium redox flow battery.

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1. Introduction

Increasing attention has been provided to the development of sustainable utility-scale energy storage and conversion technologies in recent years [1–3]. Redox flow batteries can provide an ample supply of electrical power and allows for the management of such power. Redox flow battery systems have received considerable attention recently because they possess advanced characteristics, such as long life, flexible design, and high reliability [4–6]. In particular, the vanadium redox flow battery (VRFB) is a promising candidate for the storage of electrical energy. VRFB offers the advantage low contamination of metal cations by employing the same element in both electrolytes [7]. Although significant improvements have been made to VRFBs, these are insufficient for VRFBs to replace today's internal combustion engines. Therefore, the energy efficiency of VRFBs must be improved prior to commercialization. The energy efficiency of a VRFB depends largely on the physicochemical properties of its electrodes because the electrochemical reactions of vanadium ions occur on the electrode

surface [8,9]. Graphite felt with a large surface area is an appropriate material because it provides abundant redox reaction sites and maintains good electronic conduction as well as mechanical stability during cycles. A typical electrode material for VRFB is graphite felt, which exhibits good stability in highly acidic solutions and provides a large reactive surface area for a sufficient number of redox reaction sites [10]. However, graphite felt must be subjected to surface treatments before they can be utilized as electrodes to ensure that their electrochemical activity and wettability originated from a hydrophobic surface [11,12].

Several treatments have been adopted at various conditions to make the surface of graphite felt electrodes more active. An effective way to achieve this is the introduction of an electrocatalyst on the surface of graphite felt to reduce activation over potential for the chemical conversion of electro-active species [13].

The electrochemical activity of vanadium redox couples can be facilitated by the electrodeposition of noble metal catalysts, such as Pt, Pd, Au, and Ir [14,15]. However, the high cost and poor mechanical stability of noble metal catalysts remain unresolved. An efficient synthetic process for introducing catalysts onto the surface of graphite felt must therefore be developed. Advanced catalysts with low cost and high catalytic activity have been studied by some

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researchers, e.g., Yao et al. [2] demonstrated carbon paper electrode coated with WO_3/SAC was developed to improve the electrochemical performance toward VRFB, and Kim et al. [13] reported that Mn_3O_4 modified carbon felt electrodes produced efficient operation of a VRFB.

Moreover, M. Skyllas-Kazacos [16] showed that use of Pb ions in the electrolyte would deposit (as PbO_2) on the positive electrode during cycling and catalyze the positive half-cell reactions. The same patent also suggested that Pb ions in the VRB electrolyte would deposit on the negative half-cell electrode and suppress hydrogen evolution during charging. The main advantages of using lead dioxide (PbO_2) as a novel catalyst are low price compared with noble metals, chemical stability in corrosive media, and high overpotential value for oxygen evolution reaction [17–19]. The electrochemical deposition of PbO_2 often occurs in an acidic medium. Tetragonal $\beta\text{-PbO}_2$ is formed in such conditions; thus, the term “ PbO_2 ” in applied electrochemistry usually refers to the β -form [20]. A coating prepared in an acidic medium does not adhere sufficiently to the substrate; additives, such as sodium lauryl sulfate, are therefore added to the electrolyte [21]. The second common type of lead dioxide, orthorhombic $\alpha\text{-PbO}_2$, can be deposited from an alkaline solution (e.g., sodium acetate, lead acetate, and KOH). $\alpha\text{-PbO}_2$ has a more compact structure compared with porous $\beta\text{-PbO}_2$ [22], resulting in better contact between particles.

Thus, we propose the use of PbO_2 as a novel catalyst and replacement for noble metal catalysts to improve the electrochemical activity of graphite felt electrodes in VRFB. PbO_2 was loaded on graphite felt through pulse electrodeposition for the first time to prepare a composite graphite felt electrode. Pulse electrodeposition has many advantages, such as small pulse current electrodeposition coating crystal, improvement of deep and even plating to obtain compact and uniform coating, and higher deposition rate and current efficiency than electrochemical deposition [23]. $\alpha\text{-PbO}_2$ coating was produced through pulse electrodeposition in an alkaline lead bath on graphite felt; it served as the binder, atop which $\beta\text{-PbO}_2$ was electrodeposited from an acidic lead bath. Surface morphology and crystal structure were analyzed through scanning electron microscopy (SEM) and X-ray diffraction (XRD). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to evaluate the electrochemical activity of the as-prepared electrodes. Dynamic flowing single cell test was then performed.

In our research, the positive electrode for VRFB was mainly studied. In order to eliminate the influence of the negative electrode on cell potential, we used the graphite felt loaded with PbO_2 as the positive electrode and used the hydrogen electrode and H_2 to replace the graphite felt and $\text{V}^{2+}/\text{V}^{3+}$ couple in the negative electrode in the VRFB performance test.

2. Experimental

2.1. Preparation and characterization of PbO_2 -modified graphite felt

2.1.1. Preparation of PbO_2 -modified graphite felt

Commercial graphite felt was used particularly for this study (3 mm thickness PAN-based graphite felt, $<16 \text{ m}\Omega \text{ cm}^2$, Hongwei Co., Gansu). The pristine graphite felt was pretreated at a constant temperature of 400°C for 30 h in a muffle oven before use (referred to as bare graphite). PbO_2 was pulse electrodeposited on bare graphite felt with a battery test system, LAND CT2001C (LAND Electronics Co., Wuhan). The preparation procedures were mainly for $\alpha\text{-PbO}_2$ preliminary deposition. Electrochemical deposition of $\alpha\text{-PbO}_2$ was carried out in an alkaline lead bath (referred to as S_1 hereafter) as reported by other researchers [20]. NaOH solution (3.5 M) was saturated with litharge PbO at 40°C for 15 min at a

current density of 3 mA cm^{-2} . The pH of S_1 is >14 , and the soluble Pb (II) species are HPbO_2^- anions.

The graphite felt with $\alpha\text{-PbO}_2$ was washed with distilled water until the pH of the rinse water became neutral. The top coating ($\beta\text{-PbO}_2$) was electrodeposited on the graphite felt loaded with $\alpha\text{-PbO}_2$ from an acidic lead bath (referred to as S_2 hereafter) [24]. $\beta\text{-PbO}_2$ was electrodeposited at 40°C in 0.03 M HNO_3 solution containing 0.23 M $\text{Pb}(\text{NO}_3)_2$ and 0.03 M NaF for 15 min. The current density was 30 mA cm^{-2} . The pH of S_2 was 2. The duration of pulse electrodeposition was 30 min. All experiments were performed in a two-electrode configuration with Pt foil as cathode and graphite felt ($0.3 \times 3 \times 4 \text{ cm}^3$) as anode. The electrodes were removed from the depositing solutions and rinsed with distilled water after deposition. The average measured amount of PbO_2 on the graphite felt was 0.03 g cm^{-3} . During the experiments, the current was maintained for 5 s after every 10 s. Analytical grade reagents and distilled water were utilized for all solutions. Another bare graphite felt was prepared for comparison.

2.1.2. Characterization of PbO_2 -modified graphite felt

2.1.2.1. SEM for PbO_2 -modified graphite felt. The morphology of the materials was analyzed with a JSM-6360LV microscope (JEOL, Japan) at an accelerating voltage of 20 kV. The microscope was also utilized to examine the appearance of the PbO_2 -modified graphite felt at 20 kV.

2.1.2.2. X-ray diffraction for PbO_2 -modified graphite felt. The morphology and microstructure of the graphite felt modified with PbO_2 were characterized with an X-ray diffractometer (EMPYREAN, PANalytical Co., Netherlands) with $\text{K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) in the 2θ range of 10° – 90° . The X-ray tube was operated at 40 kV with a Cu target.

2.1.2.3. Cyclic voltammetry and electrochemical impedance spectroscopy for PbO_2 -modified graphite felt. The electrochemical activity of the as-prepared electrodes was evaluated through CV and EIS. CV and EIS results were obtained in the electrochemical workstation, Autolab PGSTAT302N (Ecochemie Co., Netherlands) in 0.5 M $\text{VOSO}_4 + 3 \text{ M H}_2\text{SO}_4$ solutions at room temperature. A three-electrode system was utilized in the electrochemical test with PbO_2 -modified graphite felt as the working electrode; saturated calomel electrode (SCE) and Pt foil were employed as the reference and counter electrode, respectively. Salt bridge with Rudin capillary was used to connect the reference and working electrodes. The scanning range of CV was limited within 0 V–1.6 V (vs. SCE), and the scanning rate was 2 mV s^{-1} . Impedance spectra were obtained by sweeping various frequencies in the range of 10^{-2} Hz to 10^5 Hz . The potential was fixed at 0.79 V in all EIS measurements to ensure similar polarization.

2.2. Single cell evaluation

Constant current charge–discharge tests were performed with a single cell and CT2001D LAND battery test system (LAND Electronics Co., Wuhan). A piece of PbO_2 -modified graphite felt with an active area of 12 cm^2 ($3.0 \text{ cm} \times 4.0 \text{ cm}$) was used as a positive electrode. Nafion 1135 ion exchange membrane was utilized as the separator. A graphite plate with a serpentine flow field on its surface served as the current collector. The cell was sealed with rubber washers. The initial positive electrolyte was 100 mL 0.5 M $\text{V}(\text{IV}) + 3 \text{ M H}_2\text{SO}_4$ solution, which was stored in tanks outside the cell. The electrolytes were pumped into the compartments as flowing liquid during cell operation. The upper limit of charge voltage and lower limit of discharge voltage were 1.7 and 0.8 V,

respectively. The hydrogen electrode and H_2 replaced the graphite felt and V^{2+}/V^{3+} couple in the negative side.

Another Single cell with bare graphite felt was used as a positive electrode was prepared for comparison.

3. Results and discussions

3.1. Morphologies of PbO_2 -modified graphite felt

The morphologies of the PbO_2 -modified graphite felt prepared through pulse electrodeposition were estimated from the SEM photographs. The results are shown in Fig. 1(a) and (b). The average particle size of PbO_2 is 2 μm , and particulates are well distributed on graphite felt (Fig. 1(b)).

3.2. X-ray diffraction for PbO_2 -modified graphite felt

X-ray diffraction experiments were performed with the sample to confirm the presence of the two varieties of PbO_2 in the electrodes. Fig. 2 shows the XRD of pulse electrodeposited PbO_2 in the graphite felt electrode. β - PbO_2 can be identified by its intense lines, namely, (110 at 25.19° , 2θ), (101 at 31.68° , 2θ), (211 at 48.93° , 2θ), and (301 at 62.1° , 2θ). Likewise, α - PbO_2 can be identified by its (111 at 28.34° , 2θ), (200 at 35.98° , 2θ), (021 at 33.9° , 2θ), and (110 at 23.09° , 2θ) lines, which are in the order of decreasing diffraction intensity. All reflections match the typical XRD patterns of PbO_2 (JCPDS#73-0851 and 72-2102) well. Previous studies reported that lead dioxide electrodeposited from an acidic $Pb(NO_3)_2$ solution

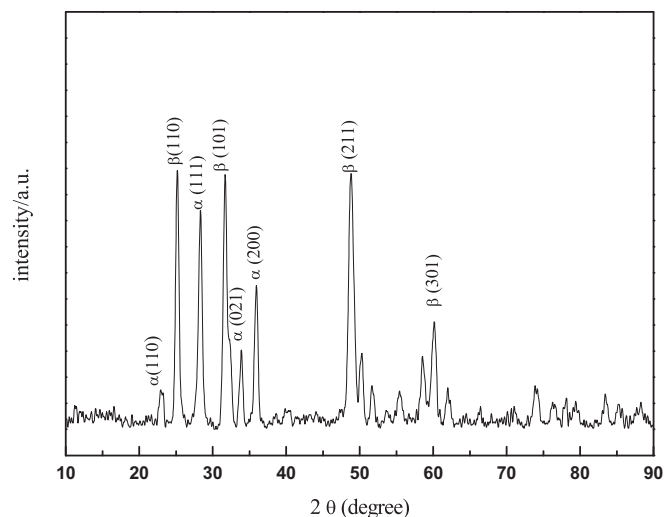


Fig. 2. XRD pattern of PbO_2 nanoparticles precipitated on graphite felt through pulse electrodeposition.

exists in β - PbO_2 form, whereas that from an alkaline solution normally exists in α - PbO_2 form [25,26]. These results prove that PbO_2 films consist of a mixture of orthorhombic α and tetragonal β - PbO_2 crystallographic phases.

3.3. Cyclic voltammetry and electrochemical impedance spectroscopy for PbO_2 -modified graphite felt and bare graphite felt

The cyclic voltammograms of graphite felt electrodes modified with PbO_2 and bare graphite felt electrodes are compared in Fig. 3. The oxidation and reduction peaks corresponding to a $V(V)$ – $V(IV)$ couple appear at approximately 1.2 and 0.6 V (vs. SCE), respectively. The peak currents of the oxidation and reduction of $VO^{2+} \rightleftharpoons VO_2^+$ on graphite felt modified with PbO_2 are 80.16 and -57.2 mA cm^{-2} , respectively, whereas the peak currents for bare graphite felt are 44.41 and $-32.39 \text{ mA cm}^{-2}$, respectively. These results can be attributed to the well-dispersed PbO_2 nanoparticles that served as an electrocatalyst for the redox reactions of $V(V)$ – $V(IV)$. Therefore, the coulomb efficiency of a VRFB that employs graphite felt

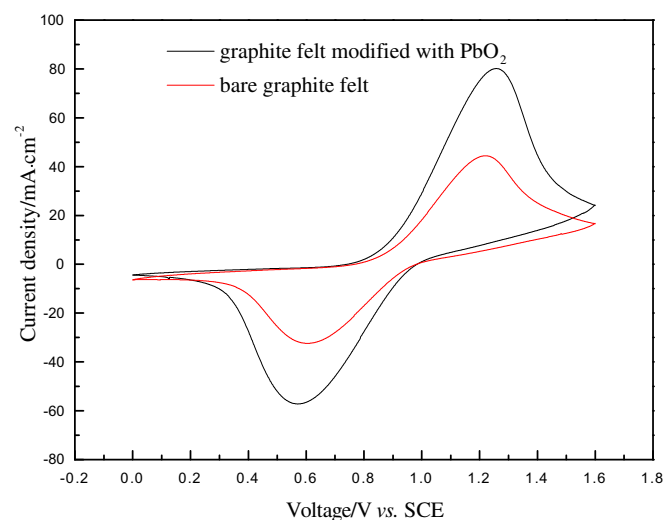


Fig. 3. Cyclic voltammograms of graphite felt modified with PbO_2 and bare graphite felt.

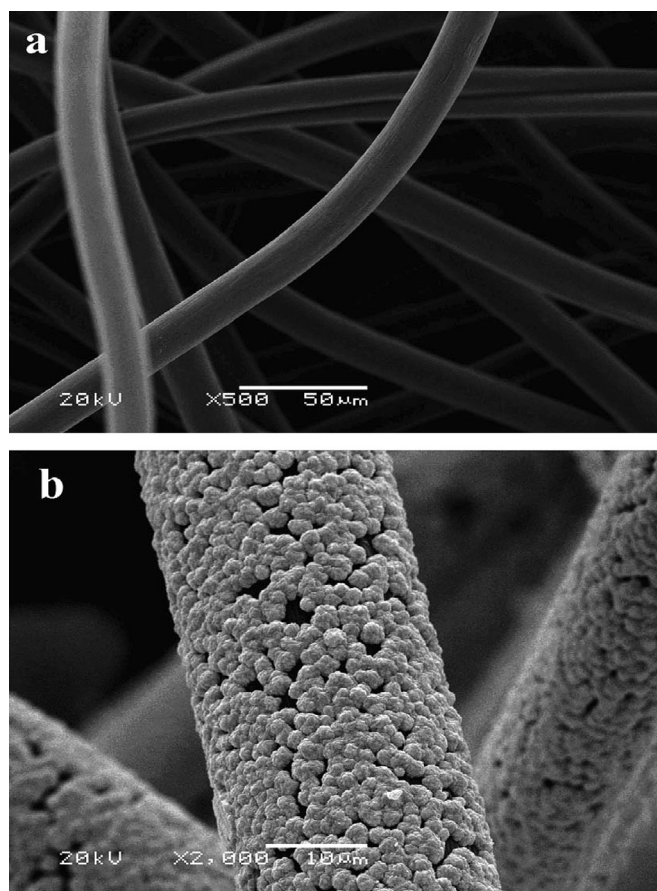


Fig. 1. SEM photographs of graphite felt. (a) Bare graphite felt and (b) graphite felt modified with PbO_2 through pulse electrodeposition.

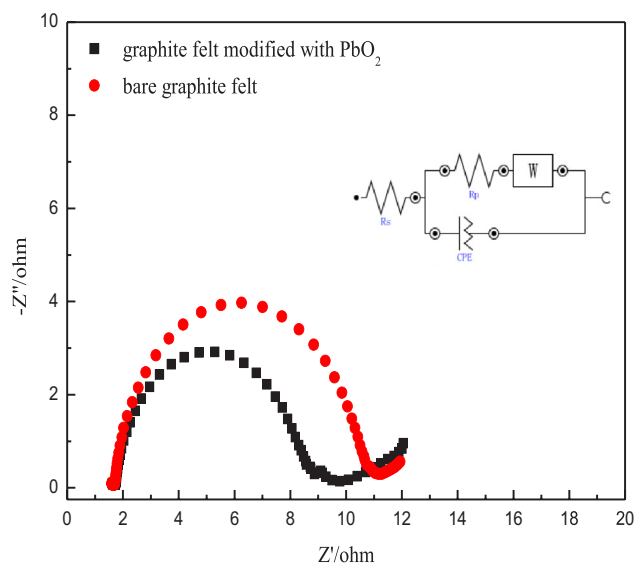


Fig. 4. Electrochemical impedance spectra of graphite felt modified with PbO₂ and bare graphite felt.

modified with PbO₂ can be significantly enhanced by boosting the chemical conversion of the electro-active species. The Nyquist complex-plane impedance plots of graphite felt with and without PbO₂ are shown in Fig. 4. The plots exhibit a similar pattern: a depressed capacitive semi-circle in the high-frequency region and a sloping straight line in the low-frequency region. The inset in Fig. 4 shows the equivalent circuit derived from the Nyquist plots. The derived circuit is employed to quantitatively describe the change in impedance. R_s is bulk solution resistance, R_p is Faradaic interfacial charge-transfer resistance, CPE is the constant phase element that accounts for double-layer capacitance, and W is Warburg impedance. The bulk solution resistance of graphite felt with and without the PbO₂ has similar values of 0.16 Ω ; the corresponding charge-transfer resistance is 7.27 and 9.12 Ω , respectively (deduced from the inset in Fig. 4). This result implies that the addition of PbO₂ causes charge-transfer resistance to decline, reflecting higher reactive velocity. Thus, the performance of VRFB is enhanced when the cell anode is modified with PbO₂. And these results also verify the use of Pb ions to catalyze the electrode reactions of VRFB [16].

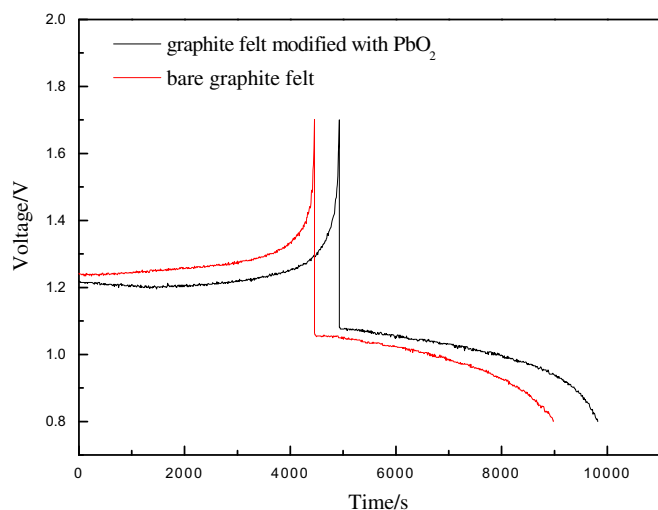


Fig. 5. Charge–discharge profiles of cells with and without PbO₂ at a current density of 70 mA cm⁻².

Table 1

Parameters obtained by fitting the charge and discharge curves in Fig. 5.

Cells	Initial charge voltage (V)	Initial discharge voltage (V)	Voltage efficiency (%)	Charge capacity (mA h)	Discharge capacity (mA h)
With PbO ₂	1.22	1.08	82.4	1167.0	1161.1
Without PbO ₂	1.24	1.06	79.8	1014.8	954.4

3.4. VRFB single cell performance

Charge–discharge testing was conducted with a VRFB cell to further understand the effect of surface modification with PbO₂ on the electrochemical performance of graphite felt. Fig. 5 presents the charge–discharge curves of two cells with PbO₂-modified graphite felt and bare graphite felt at a current density of 70 mA cm⁻². The curve of the cell with PbO₂-modified graphite felt as its electrode has a low charge voltage plateau and high discharge voltage plateau, thereby achieving very high voltage efficiency because the catalysis of PbO₂ reduced the electrochemical polarization of the redox reaction. For the same reason, the cell with PbO₂-modified graphite felt exhibited high charge and discharge capacities. The detailed data obtained from Fig. 5 are summarized in Table 1. The voltage and energy efficiency of the cell are 82.4% and 82% at a current density of 70 mA cm⁻².

The typical charge–discharge curves of the cell with PbO₂-modified graphite felt at current densities of 40, 50, 60, 70, and 80 mA cm⁻² were tested and are presented in Fig. 6. The cell maintained good charge–discharge performance at different current densities. The efficiencies of the cell are listed in Table 2. The CE, VE, and EE at 40 mA cm⁻² are 97.5%, 91.4%, and 89.1%, respectively. The current density reached 80 mA cm⁻². VE remained higher than 78.3%. Fig. 7 presents the energy efficiency data of 30 charge–discharge cycles of the cell assembled with PbO₂-modified graphite felt at 50 mA cm⁻². No reduction in performance was observed, indicating that the PbO₂ particles remained on the graphite felt under the flowing electrolyte.

4. Conclusions

Graphite felt electrodes modified by PbO₂ composed of a mixture of orthorhombic α and tetragonal β -PbO₂ crystallographic phases were prepared through pulse electrodeposition and were then applied to a VRFB for the first time. Analysis of the

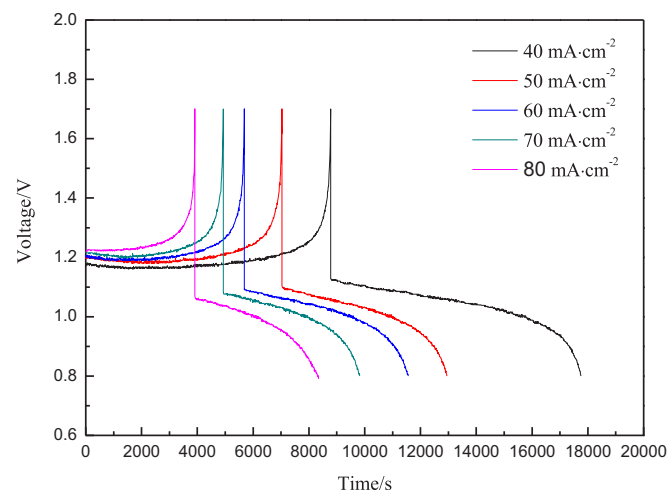


Fig. 6. Charge–discharge profiles of the cell with PbO₂ at current densities of 40, 50, 60, 70, and 80 mA cm⁻².

Table 2
Efficiencies of the cell with PbO₂ at current densities of 40, 50, 60, and 70 mA cm⁻².

Current density (mA cm ⁻²)	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
40	97.5	91.4	89.1
50	98.4	88.9	87.5
60	99.1	86.1	85.3
70	99.5	82.4	82.0
80	99.7	78.3	78.1

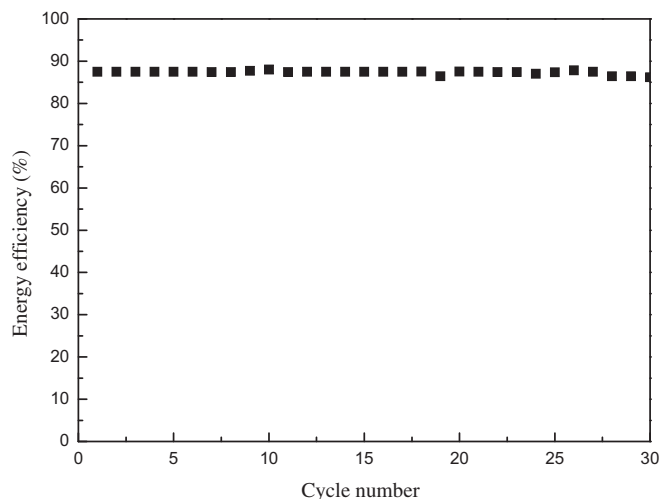


Fig. 7. Energy efficiency data of 30 charge–discharge cycles of the cell with PbO₂ at 50 mA cm⁻².

electrochemical performance of the VRFB demonstrated the promising electro-catalytic effect of PbO₂. The electrochemical activity of graphite felt modified with PbO₂ for vanadium redox couples was notably improved, and charge transfer resistance was reduced significantly because of the catalytic effect of PbO₂ particles dispersed on the surface of the graphite felt. Thus, single cell performance improved remarkably with the use of the PbO₂-coated graphite felt electrode. The CE, VE, and EE of the cell at a current density of 70 mA cm⁻² are 99.5%, 82.4%, and 82.0%, respectively; these values are much higher than those of the cell assembled with bare graphite felt. No decrease in energy efficiency was observed after 30 charge–discharge cycles at 50 mA cm⁻². These results

suggest that simple surface modification with non-precious metal oxides is a promising method for vanadium redox flow batteries in terms of production cost as well as electrochemical properties.

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